Thermal Polymerization of 2-(Mercaptoalkyl)-2-oxazolines

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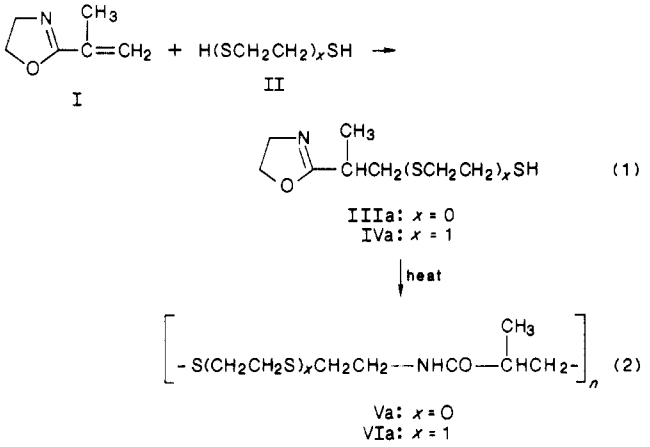
ABSTRACT: 2-(Mercaptoalkyl)-2-oxazolines were synthesized by addition of H_2S and 1,2-ethanedithiol to 2-isopropenyl-2-oxazoline. Thermal polymerization of the 2-(mercaptoalkyl)-2-oxazolines, referred to as IPOH_2S and IPOEDT adducts, respectively, was studied over the temperature range 100–200 °C in bulk and in DMF solution. The polymer structures were identified as poly[(1-thia-4-aza-5-oxo-1,5-pentanediyl)propylene] and poly[(1,4-dithia-7-aza-8-oxo-1,8-octanediyl)propylene], respectively (subsequently referred to as IPOH_2S and IPOEDT polymers), on the basis of ^{1}H and ^{13}C NMR and IR. Size exclusion chromatography (SEC) showed $\bar{M}_n$ to vary in the range 4100–42900 depending on the reaction conditions. A polymerization mechanism is proposed on the basis of ring-opening nucleophilic attack of sulfur on the CH_2–O bond (5-position) of the oxazoline ring.

Introduction

The cationic[1-3] and zwitterionic[4,5] ring-opening polymerization of 2-oxazolines has received considerable attention. The thermal polymerization of 2-(mercaptoalkyl)-2-oxazolines was reported by Tomalia and co-workers in a patent[6] and colloquium.[7] Few details of the reaction have been published, although Wehrmeister[8] reported the ring-opening addition of thiophenol to 2-alkyl-2-oxazolines. In this paper we report the synthesis of 2-(2-oxazolin-2-yl)propanethiol (III) and 2-[(2-[2-oxazolin-2-yl]propyl)-thio]ethanethiol (IV) by the addition of H_2S and 1,2-



ethanedithiol, respectively, to 2-isopropenyl-2-oxazoline (IPO) and their subsequent thermal polymerization to poly[(1-thia-4-aza-5-oxo-1,5-pentanediyl)propylene] and poly[1,4-dithia-7-aza-8-oxo-1,8-octanediyl)propylene], respectively: III and V will be referred to as IPOH_2S adduct and IPOH_2S polymer, respectively, and IV and VI as IPOEDT adduct and IPOEDT polymer, respectively, throughout this paper.

Experimental Section

Materials. 2-Isopropenyl-2-oxazoline (IPO) (Dow Chemical), 1,2-ethanedithiol (EDT) (Aldrich), and solvents (DMF, CH_3CN) were dried over 3-Å molecular sieves and then distilled under reduced nitrogen atmosphere. The middle fractions were collected and stored in the refrigerator prior to use. IPO undergoes vinyl polymerization when stored at ambient temperature (ca. 10% in 3 weeks). Hydrogen sulfide (Matheson) was used as received.

Adduct Preparation and Polymerization. The 1:1 adducts of IPO with EDT and hydrogen sulfide were formed and then polymerized in bulk and solution. All sample preparations and manipulations for the polymerization experiments were carried out in a drybox under nitrogen. Sample tubes were subsequently sealed under vacuum prior to polymerization. 3,5-Di-*tert*-butyl-4-hydroxyanisole (BHA) was added at a concentration of 0.25 mol % as a radical inhibitor in most experiments.

IPOEDT. For solution polymerization, equimolar amounts of IPO and EDT were each separately dissolved in DMF at about 30% concentration. The EDT solution was placed in a round-bottom flask cooled with ice–water and the IPO solution added from an addition funnel with stirring over a period of about 1 h. The reaction mixture was gradually warmed to room temperature and then allowed to set for 1.5–2 h. Aliquots of this solution containing the IPOEDT adduct were transferred to polymerization tubes, sealed under vacuum (ca. 1 Torr), and then reacted at the desired reaction temperature. For bulk polymerization, IPO and EDT were mixed in acetonitrile at 0 °C, transferred to polymerization tubes, and solvent evaporated at room temperature, the tubes were sealed under vacuum, and then reaction was carried out at the desired temperature.

IPOH_2S. Absolute ethanol (100 mL) was added to a 250-mL three-neck flask fitted with an addition funnel, gas inlet, and condenser after flushing with dry nitrogen. The flask was cooled with an ice–salt bath while hydrogen sulfide was bubbled through the ethanol for 15 min. While a slow flow of hydrogen sulfide was maintained, a solution of 10.0 g of IPO in 25 mL of absolute ethanol was added dropwise over a period of about 1.5 h with stirring and cooling. Hydrogen sulfide addition was continued for about 0.5 h and the reaction mixture warmed slowly to 35 °C and maintained at that temperature for 1 h. Dry nitrogen was passed through the reaction mixture to expel excess hydrogen sulfide and then ethanol distilled off at 40 °C under vacuum. The yellow liquid residue was distilled in a short-path distillation apparatus under vacuum to yield the IPOH_2S adduct as a colorless liquid, bp 51 °C (0.01 Torr), in 80% yield. The purified adduct was used in bulk and solution polymerizations.

Some polymerizations were carried out to specific reaction times and the reaction mixtures analyzed directly by SEC. Other polymerizations were carried out to long reaction times and the polymers isolated and analyzed by SEC, IR and NMR. Polymer isolation was performed for both the IPOEDT and IPOH_2S systems in the same manner. The reaction mixture from solution polymerization in DMF was poured into a 15-fold excess of diethyl ether at room temperature to precipitate the product. The ether was decanted and the polymer washed with ether and then dried overnight in a vacuum oven at 40 °C. The reaction mixture from bulk polymerization was dissolved in DMF and purified in the same manner. All polymerization reactions proceeded with near quantitative conversion (>98%) of adduct to polymer.

Spectroscopic Analysis. IR spectra of the polymers were recorded on a Beckmann 4260 IR spectrometer using thin-film samples on NaCl plates. The polymer was deposited as a thin film on a NaCl plate from 1,1,2,2-tetrachloroethane and DMF solutions for the IPOEDT and IPOH_2S polymers, respectively; the solvent was evaporated in a vacuum oven (ca. 1 Torr) at 45 °C overnight. ^{1}H (200.1 MHz) and ^{13}C (50.3 MHz) NMR spectra were recorded on an IBM WP 200SY FTNMR spectrometer using

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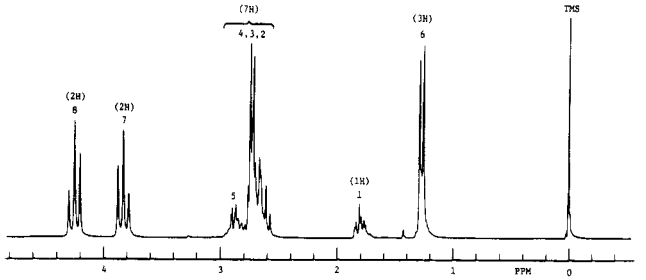


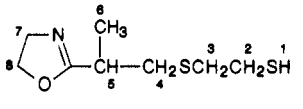
Figure 1. 200.1-MHz ^1H NMR spectrum of IPOEDT adduct in $CDCl_3$.

a 5-mm dual $^{13}C/^1H$ probe. ^1H NMR of the adducts and polymers were obtained at 25 °C with 10% (w/v) solutions in $CDCl_3$ and 7% (w/v) solutions in Me_2SO-d_6, respectively. ^{13}C NMR spectra were obtained by using 10–15% (w/v) solutions in Me_2SO-d_6, $CDCl_3$, trifluoroacetic acid with D_2O capillary, and 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2). Me_4Si was used as an internal standard for both ^1H and ^{13}C NMR. The acquisition parameters for ^1H NMR were 30° pulse angle, 10-s total delay between pulses, and 128–256 total acquisitions. The acquisition parameters for ^{13}C NMR were 30° pulse angle, 2.5-s total delay between pulses, and 1000–20000 total acquisitions. Data were acquired and Fourier transformed in 16K.

Molecular Weight Measurements. Size exclusion chromatography (SEC) of the various polymer samples was carried out at 80 °C on a Waters 150 C instrument with 840 workstation using DMF containing 0.05 M LiBr as the mobile phase at a flow rate of 1.0 mL/min. The presence of LiBr prevented absorption of the polymer on the stationary phase. The stationary phase consisted of a set of four ultrastryagel columns of 10^5, 10^4, 10^3, and 5×10^2 Å sizes. The SEC calibration was based on polystyrene standards. Light scattering and dn/dc measurements of polymer samples in DMF at 25 °C were performed by using the LDC/Milton Roy KMX-6 LALLS and KMX-17 differential refractometer instruments.

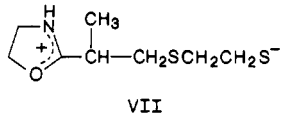
Results and Discussion

2-Isopropenyl-2-oxazoline–1,2-Ethanedithiol System (IPOEDT). Synthesis and Identification of IPOEDT Adduct. The reaction of 2-isopropenyl-2-oxazoline (IPO) and 1,2-ethanedithiol (EDT) in DMF at room temperature is fast and forms the 1:1 adduct IV (referred to as IPOEDT adduct) in quantitative yield (eq 1). The reaction was monitored by ^1H NMR by following the decay of the methyl (singlet, 1.98 ppm) and olefinic (singlets, 5.43 and 5.75 ppm) signals of IPO. Reaction between IPO and EDT was complete in 1 h as indicated by complete disappearance of ^1H NMR signals due to IPO. The ^1H NMR (Figure 1) of the IPOEDT adduct is consistent with structure IV with signal assignments shown in IVb. The SH proton



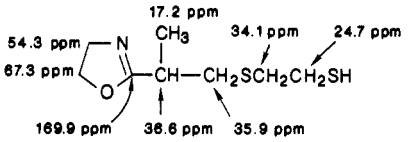
IVb

signal showed a solvent dependency—appearing as a multiplet at 1.75 ppm in $CDCl_3$ and a singlet at 2.45 ppm in Me_2SO-d_6. The ^1H NMR spectrum showed no indication of proton transfer from SH to N to form the zwitterion VII.



VII

It was anticipated that a 2:1 adduct of IPO and EDT might be formed as a byproduct of the IPOEDT adduct preparation. ^1H NMR was not useful for detecting the presence of the 2:1 adduct. Thin-layer chromatography (TLC) indicated the presence of one major component and two minor components. The minor components were identified as EDT and the 2:1 adduct by comparison with the TLC of authentic samples. (The 2:1 adduct was synthesized by reacting EDT with an excess of IPO.) ^{13}C NMR provided further evidence for the presence of the 2:1 adduct and EDT in the IPOEDT adduct. ^{13}C NMR signals for the IPOEDT adduct were assigned as shown in IVc. The 2:1 adduct was detected by the presence of



additional signals at 32.49 and 36.06 ppm for the two different methylene carbons adjacent to sulfur. The presence of EDT was shown by the methylene carbon signal at 28.60 ppm. It was esimated that the IPOEDT preparation contained a combined total of about 10% of the 2:1 adduct plus EDT. Attempted purification of IPOEDT by vacuum distillation resulted in polymerization of IPOEDT. Polymerization experiments were carried out on the IPOEDT without further purification. Although the 2:1 adduct and EDT were present along with IPOEDT, the overall polymerization reaction was not affected since the mixture contained stoichiometric amounts of thiol and 2-oxazoline functional groups.

Solution Polymerization. Solution polymerization of IPOEDT in DMF was carried out between 100 and 160 °C. The polymers, ranging from colorless gummy materials obtained at the low temperatures to solid polymers at high temperatures, were soluble in DMF, Me_2SO, and 1,1,2,2-tetrachloroethane.

The effects of reaction time, temperature and IPOEDT concentration on polymer molecular weight were studied. Molecular weights were determined by direct analysis of the reaction mixtures by SEC (based on calibration with polystyrene standards), and the results are summarized in Table I. The polymer molecular weight increased with increasing reaction time, reached a maximum after about 60 h, and remained unchanged even after 10 days at 160 °C. Figure 2 shows the SEC plots for reaction times of 5 and 60 h. (The very low molecular weight portion (43–49 min elution time) of the SEC plot was very complicated due to the presence of peaks for LiBr and water. This precluded SEC detection of IPOEDT adduct, 2:1 adduct, and EDT.) The SEC plot for the 5-h reaction time showed the presence of a number of fractions which presumably were polymer molecules of varying size from dimer upward. Longer reaction times decreased these fractions simultaneous with the appearance of a higher molecular weight fraction. The SEC plot for the 60-h reaction time showed essentially a unimodal molecular weight distribution for the high molecular weight polymer; there was only a small amount of the low molecular weight fractions. The reaction mixture showed an increase in $\bar{M}_w/\bar{M}_n$ from 1.9 to 2.2 with increasing reaction time. The results indicated that polymerization of IPOEDT adduct showed the characteristics of a step-reaction polymerization system.

The polymer molecular weight increased with increasing reaction temperature. The polymerization is very slow at temperatures below 100 °C. The most significant increase in molecular weight was observed when the monomer concentration was increased from 10 to 50% (w/w). Purification of the higher molecular weight polymers ($\bar{M}_n$ of reaction mixture > 10000) by precipitation of the reaction mixture in diethyl ether did not alter $\bar{M}_n$; low molecular weight ether-soluble fractions were absent.

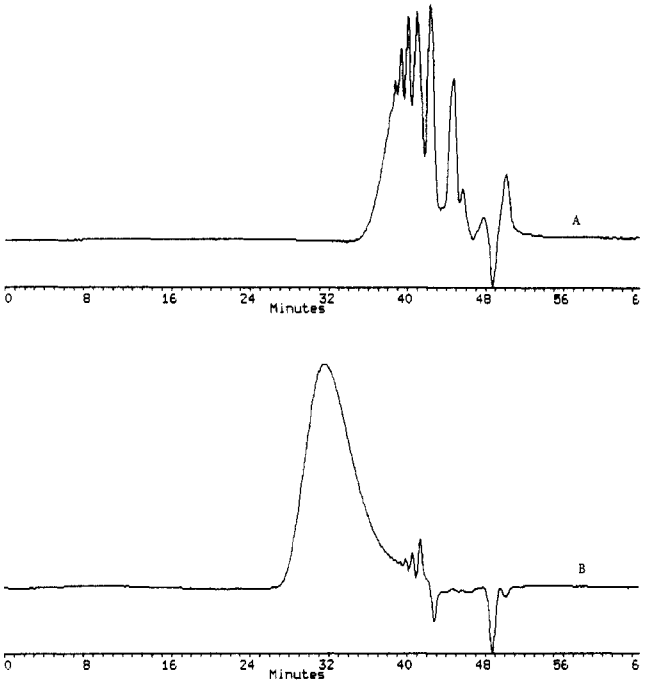


Figure 2. SEC of IPOEDT reaction mixture after polymerization in DMF solution at 160 °C: (A) after 5 h; (B) after 60 h.

Table I
Effect of Temperature, Time, and Concentration on Solution Polymerization (DMF) of IPOEDT Adduct

	mol wt by SEC[a]	
	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
temp,[b,c] °C		
100	4100	1.4
120	9700	1.5
140	16700	1.7
160	18400	1.9
time,[b,d] h		
5	1900	1.9
20	9800	1.5
60	16700	1.7
120	20000	1.9
240	18900	2.2
concn,[c,d] w/w %		
10	9100	1.5
30	16700	1.7
50	26300	2.1
70	36000	2.0

[a] SEC of unpurified reaction mixture. [b] IPOEDT adduct concentration: 30%. [c] Reaction time: 120 h. [d] Reaction temperature: 160 °C.

Bulk Polymerization. Bulk polymerization of the IPOEDT adduct was studied in the 100–200 °C temperature range. The polymers obtained were only partially soluble in solvents such as DMF and Me_2SO which were good solvents for the solution-polymerized product. The insoluble portion (less than one-fourth of the total product), presumably cross-linked, swelled in these solvents. Addition of a small amount (0.25 mol %) of 3,5-di-*tert*-butyl-4-hydroxyanisole (BHA) to the IPOEDT adduct yielded completely soluble products upon polymerization in all cases except for polymerization at 200 °C. On the other hand, solution polymerization produced soluble polymers irrespective of the presence or absence of BHA, and the presence of BHA did not have any effect on molecular weight.

Table II shows the SEC results for bulk polymerizations. The molecular weight increased with increasing reaction temperature, and the polymers obtained ranged from colorless gummy materials (at 100 °C) to solid polymers

Table II
Effect of Reaction Temperature on Bulk Polymerization of IPOEDT Adduct

	mol wt by SEC[b]			mol wt by SEC[b]	
temp,[a] °C	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	temp,[a] °C	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
100	10300	1.4	170	19100	1.8
140	15900	1.5	200[c]	22200	2.4

[a] Reaction time was 60 h with 0.25 mol % BHA present. [b] SEC of unpurified reaction mixture. [c] SEC of only the DMF-soluble product.

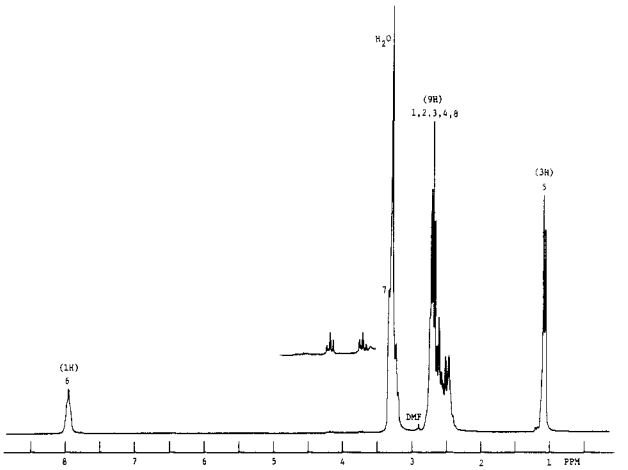
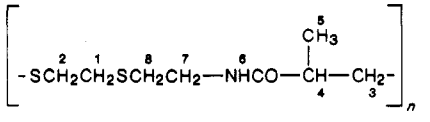


Figure 3. 200.1-MHz ^1H NMR spectrum in Me_2SO-d_6 of IPOEDT polymer synthesized by polymerization in DMF at 140 °C.

(at 140 and 170 °C) except for that produced at 200 °C. The polymer produced at 200 °C was a yellow solid and only partially soluble; the reported $\bar{M}_n$ was for the soluble portion of the product. SEC curves of the products formed at the lower temperatures showed the presence of several peaks on the very low molecular weight side indicative of the presence of dimers, trimers, tetramers, etc. Together with the $\bar{M}_w/\bar{M}_n$ values, the results indicate the step-reaction nature of this polymerization system.

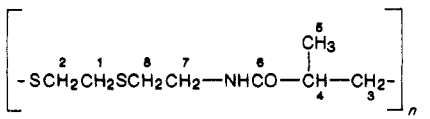
Bulk polymerization did not yield higher polymer molecular weights than solution polymerization except for solution polymerization at less than 30% adduct concentration. In fact, solution polymerization at 160 °C using a 70% adduct concentration yielded a higher molecular weight ($\bar{M}_n$ = 36000) than bulk polymerization at 170 °C ($\bar{M}_n$ = 19100).

Characterization of Polymer. The IPOEDT polymer was characterized as VI by elemental analysis and IR and NMR spectroscopy. The elemental analysis (Found: C, 46.82; H, 7.44; N, 6.74; S, 30.89) was in good agreement with that calculated for VI (Theory: C, 46.80; H, 7.36; N, 6.82; S, 31.23). Figure 3 shows the ^1H NMR spectrum of the IPOEDT polymer prepared at 140 °C in DMF with various signals assigned as shown in VIb on the basis of



VIb

the chemical shift values,[10] splitting patterns, signal areas, and deuterium exchange experiments. The ^{13}C NMR (Figure 4) signal assignments shown in VIc were based on



VIc

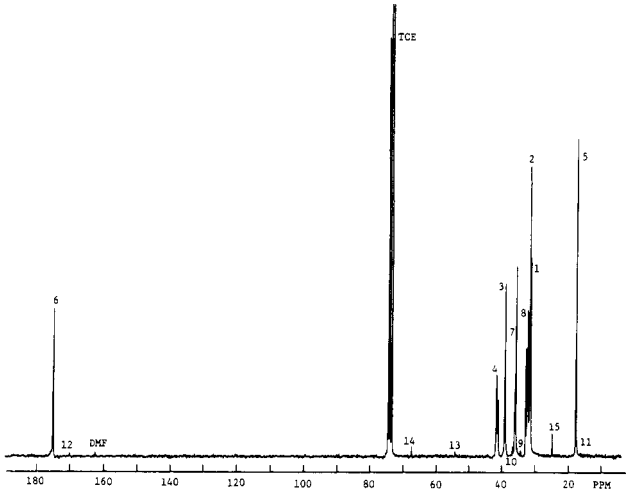
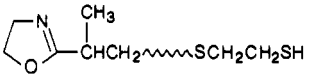


Figure 4. 50.3-MHz ^{13}C NMR spectrum in TCE-d_2 of IPOEDT polymer synthesized by polymerization in DMF at 140 °C.

chemical shift values, single-frequency off-resonance (SFOR) experiments, and the effect of temperature on the splitting of some of the signals. The ^{13}C NMR signals for carbons 4, 7 and 8 appeared as doublets when the spectrum was recorded in 1,1,2,2-tetrachloroethane-d_2 at room temperature. This signal splitting is ascribed to restricted rotation about the amide C–N bond, i.e., the presence of cis and trans isomers due to C–N double-bond character. The doublet character of the signals was temperature-dependent; the doublets coalesced into singlets at 120 °C. We have observed a similar effect for the polymer synthesized from 2-methyl-2-oxazoline and acrylic acid.[5a] Signal splitting for carbons 4, 7, and 8 was also solvent-dependent, being absent in the highly polar Me_2SO-d_6. This effect is analogous to the work of Naider and coworkers,[10] who reported from ^{13}C NMR data that the peptide Boc-Pro-Pro-Ala existed exclusively as the trans isomer at the Boc-Pro amide linkage in D_2O but as a 40:60 cis–trans mixture in the less polar $CDCl_3$. Overall, both ^{13}C and ^1H NMR results are consistent with the proposed structure VI for the polymer. Polymers synthesized under different conditions, in both bulk and solution polymerizations, showed the same repeat unit.

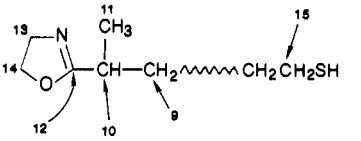
The infrared spectrum of the IPOEDT polymer showed major absorption bands at 3300, 3080 (N—H), 2962, 2934, 2870 (C—H), 1650 (C=O), 1550 (amide II), 1245 (C—N), 1229 and 1197 (SCH_2) cm^{-1} in agreement with those of structure VI.

Polymer End Groups. The polymer end groups were identified as 2-(2-oxazolin-2-yl)propyl and 2-mercaptoethyl (subsequently referred to as oxazoline and thiol end groups, respectively) as shown in VIIIa where ~~ represents the



VIIIa

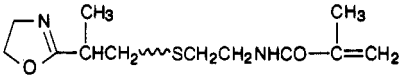
repeat unit of the polymer (structure VI). The ^1H NMR spectrum (Figure 3) of the purified polymer showed signals at 1.18 (d), 3.75 (t) and 4.20 (t) ppm for the methyl, NCH_2, and OCH_2 protons, respectively, of the oxazoline end group. The CH_2S protons of the thiol end group, expected at about 2.45 ppm on the basis of spectrum of IPOEDT adduct, could not be seen as this region of the spectrum was too crowded with signals for CH_2 protons of the repeat unit. The presence of thiol end groups was verified by reacting the polymer with excess IPO. The reaction of IPO with thiol end groups doubled the number of oxazoline end groups per polymer molecule as detected by ^1H NMR. Signals in the ^{13}C NMR spectrum (Figure 4) also supported the oxazoline and thiol end group assignments as shown in VIIIb. ^{13}C NMR data on the IPOEDT adduct was used



VIIIb

in making the end group signal assignments. Additional verification of the thiol end groups was obtained from the ^1H NMR spectrum of the acetylated polymer which showed a signal at 1.83 ppm assigned to $-S-CO-CH_3$ protons. The acetylated polymer also showed a small signal at 2.00 ppm which was assigned to $-O-CO-CH_3$ protons, indicating the presence of $-CH_2OH$ end groups. Furthermore, the ^1H NMR spectrum of the parent polymer showed a weak signal at 4.65 ppm (which disappeared upon the addition of D_2O) which could be assigned to OH protons. The amount of CH_2OH end groups decreased with increasing polymerization temperature.

The IPOEDT polymers synthesized in solution at a temperature of 140 °C or higher possessed an additional end group. The ^1H NMR spectrum indicated a $-C(CH_3)=CH_2$ end group (referred to as olefinic end group) in structure IX, where ~~ represents the polymer repeat



IX

unit (structure VI). The olefinic end group was identified by the presence of two olefinic $CH_2=C$ singlets at 5.66 and 5.33 ppm and a methyl singlet at 1.85 ppm. The thiol signal decreased as the polymerization temperature increased. Olefinic end groups predominated at 160 °C.

The presence of olefinic end groups was more prominent in polymers prepared by bulk polymerization. Except for the polymer prepared at 100 °C, all other polymers showed signals for olefinic end groups. Olefinic and oxazoline groups were the major end groups for bulk polymers produced at 170 °C and higher. The ^1H NMR spectra of the polymers obtained by bulk polymerization at 140 and 170 °C (but not at 200 °C) also showed signals for free IPO ($CH_2=C$ singlets at 5.70 and 5.47 ppm, OCH_2 triplet at 4.17 ppm, NCH_2 triplet at 3.69 ppm, CH_3 singlet at 1.92 ppm). The presence of IPO among the reaction products was verified by purifying the polymer by precipitation into ether in which IPO is soluble. The IPO signals were absent in the ^1H NMR spectrum of the purified polymer.

The number-average molecular weights of two IPOEDT polymer samples were estimated from the ^1H NMR results by comparing the OCH_2 signal of the oxazoline end group with the main chain methyl signal and assuming one oxazoline end group per polymer molecule. The two samples had $\bar{M}_n$ values of 9100 and 26300 from SEC and those determined by ^1H NMR were 4200 and 10100, respectively. The large difference between $\bar{M}_n$ values from SEC and NMR is attributed to the calibration of SEC with polystyrene standards. This difference was also observed when $\bar{M}_w$ values for the higher molecular weight sample were compared from SEC and light scattering. The $\bar{M}_w$ values were 110000 and 29000, respectively.

2-Isopropenyl-2-oxazoline–H_2S System ($IPOH_2S$). Synthesis and Identification of $IPOH_2S$ Adduct. Hydrogen sulfide reacted with IPO to form the $IPOH_2S$ adduct (III) in quantitative yield. Thin-layer chromatography showed the presence of a minor amount of the

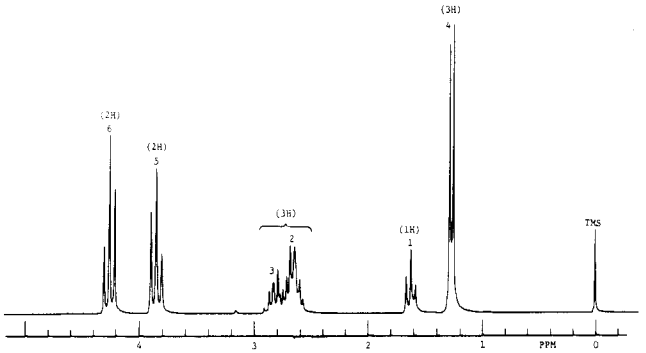


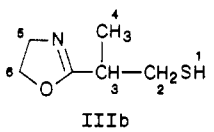
Figure 5. 200.1-MHz ^1H NMR spectrum of $IPOH_2S$ adduct in $CDCl_3$.

Table III
Effect of Concentration on Solution Polymerization (DMF) of $IPOH_2S$

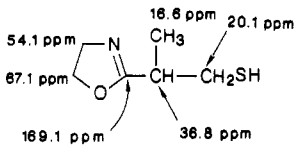
adduct concn,[a] w/w %	mol wt by SEC[b] $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	adduct concn,[a] w/w %	mol wt by SEC[b] $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
30	21 800	2.0	50[c]	36 800	1.8
50	32 300	1.9	70	42 900	2.1

[a] Reaction time and temperature were 65 h and 160 °C, respectively. [b] SEC of unpurified reaction mixture. [c] 0.25 mol % BHA present.

2:1 adduct of IPO and hydrogen sulfide. The $IPOH_2S$ adduct III was easily isolated as a pure compound by vacuum distillation, bp 51 °C (0.01 Torr). The $IPOH_2S$ adduct, a colorless liquid, is stable at room temperature but forms disulfides when exposed to air. The structure of the $IPOH_2S$ adduct was established by elemental analysis and ^1H and ^{13}C NMR. Elemental analysis (Found: C, 49.73; H, 7.96; N, 9.34; S, 21.80) was in good agreement with that calculated for structure III (Theory: C, 49.63; H, 7.63; N, 9.65; S, 22.08). Figure 5 shows the ^1H NMR spectrum of the $IPOH_2S$ adduct, and the signal assignments are shown in IIIb. Both ^{13}C and ^1H NMR were consistent with structure III for the $IPOH_2S$ adduct. The signals in the ^{13}C NMR spectrum were assigned as shown in IIIc.



IIIb



IIIc

Polymerization. Solution polymerization of the $IPOH_2S$ adduct was carried out in DMF at 160 °C with varying adduct concentration. The molecular weight, as determined by SEC, increased with increasing adduct concentration (Table III). (Several minor very low molecular weight peaks were observed at short reaction times, presumably due to dimer, trimer, and other low-mers derived from $IPOH_2S$ adduct.) The molecular weight of the purified polymer (via precipitation in diethyl ether) showed no significant change from that of the unpurified reaction mixture, indicating the absence of ether-soluble low molecular weight products.

Similar to the IPOEDT system, polymerization in bulk yielded products that were only partially soluble in solvents such as DMF and Me_2SO; the insoluble portions swelled in these solvents. The addition of BHA (0.25 mol %) to the adduct and subsequent bulk polymerization yielded completely soluble polymers. Solution polymerization always yielded soluble polymers, and the presence of BHA did not affect the polymer molecular weight. Table IV

Table IV
Effect of Temperature on Bulk Polymerization of $IPOH_2S$ Adduct

temp,[a] °C	mol wt by SEC[b] $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	temp,[a] °C	mol wt by SEC[b] $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
100	10 400	1.4	140	35 500	2.0
120	17 700	1.7	160	35 100	1.9

[a] Reaction time was 65 h with 0.25 mol % BHA present. [b] SEC of unpurified reaction mixture.

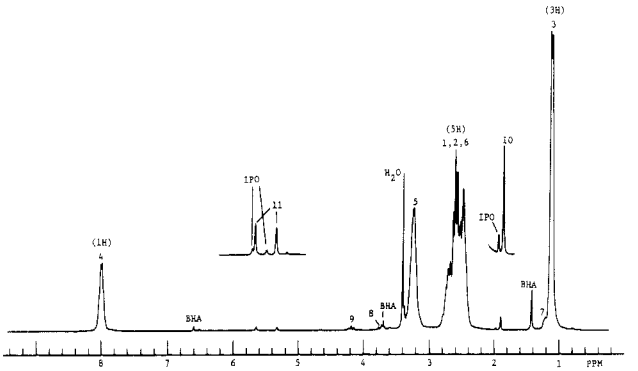
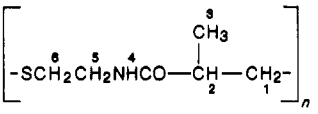


Figure 6. 200.1-MHz ^1H NMR spectrum in Me_2SO-d_2 of $IPOH_2S$ polymer (unpurified) synthesized by bulk polymerization at 140 °C.

shows the effect of temperature on the polymer molecular weight in bulk polymerization. The polymer molecular weight increased with increasing temperature reaching a maximum at 140 °C. Bulk polymerizations at the higher reaction temperatures yielded somewhat lower molecular weights than solution polymerizations at 50–70% adduct concentrations.

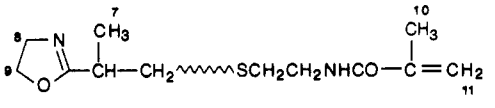
Characterization of Polymer. The $IPOH_2S$ polymer was characterized as structure V by elemental analysis and IR and NMR spectroscopy. The elemental analysis (Found: C, 49.75; H, 7.69; N, 9.52; S, 21.98) was in good agreement with that calculated for V (Theory: C, 49.63; H, 7.64; N, 9.65; S, 22.08). The infrared spectrum of the polymer showed major absorption bands at 3290, 3070 (N—H), 2962, 2922, 2870 (C—H), 1645 (C=O), 1545 (amide II), 1225 (C—N), 1250 and 1190 (SCH_2) cm^{-1} in agreement with those of structure V.

Figure 6 shows the ^1H NMR spectrum of the product (unpurified polymer) obtained in bulk polymerization at 140 °C. The major signals for the repeat unit are assigned as shown in Vb. The minor signals in the spectrum are



Vb

due to polymer end groups, BHA and free IPO. Free IPO was present in all bulk polymerized samples. The polymer end groups are assigned to oxazoline and olefinic groups as shown in X, where ~~~ represents the polymer repeat unit (structure V).



X

The polymers prepared at 140 and 160 °C in bulk showed the presence of oxazoline and olefinic groups as the major end groups. The polymer prepared in solution at 160 °C contained the olefinic group as the major end

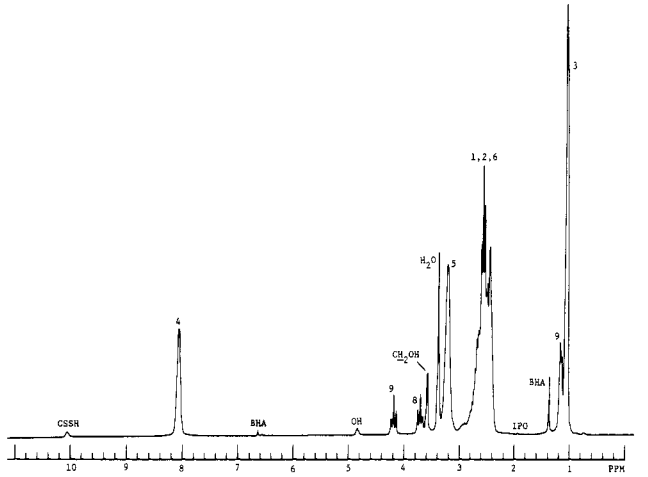
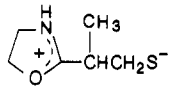


Figure 7. 200.1-MHz ^1H NMR spectrum in Me_2SO-d_6 of $IPOH_2S$ polymer (unpurified) synthesized by bulk polymerization at 100 °C.

group and oxazoline as the minor end group. The ^1H NMR spectrum of the polymers prepared in bulk at 100 and 120 °C (Figure 7) showed strong signals for the oxazoline end group, very weak signals for the olefinic end group, and weak signals at 10.05, 4.80, and 3.55 ppm for other types of end groups. The latter three signals are barely detectable for polymers synthesized above 120 °C. Two (10.05, 4.80 ppm) of the three signals exchanged rapidly with D_2O. Thiol end groups ($-CH_2SH$) were not present in any of the polymers as noted by the absence of any change in the concentration of oxazoline end groups after the polymer samples were reacted with excess IPO. The ^1H NMR signals at 4.80 and 3.55 ppm were assigned to OH and CH_2O protons, respectively, of $-CH_2OH$ end groups (analogous to the IPOEDT polymer synthesized at 160 °C). The 10.05 ppm signal was assigned to –CSSH protons. ^{13}C NMR of the polymer verified the conclusions obtained from ^1H NMR.

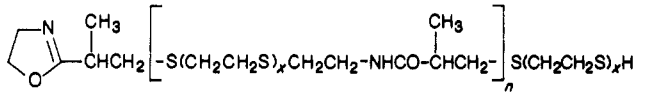
The possibility of forming zwitterion XI from $IPOH_2S$ adduct during polymerization was examined by recording the ^1H NMR spectrum of a 30% solution of the adduct in DMF-d_7 after heating at 150 °C for 15 min and 1 h.



XI

NMR signals would be expected at 8.92 (br, NH), 4.68 (OCH_2), 4.01 (NCH_2), 2.96 (CH, CH_2S) and 1.30 (CH_3) ppm if zwitterion XI were formed. The expected chemical shift values were based on the ^1H NMR spectrum observed for the $IPOH_2S$ adduct–F_3CCOOH salt (prepared by mixing the $IPOH_2S$ adduct with trifluoroacetic acid in DMF-d_7). The ^1H NMR spectrum of the $IPOH_2S$ adduct after heating for 15 min showed the appearance of signals due to polymer formation but no signals for the zwitterion; similar results were obtained after heating for 1 h. These results indicate that zwitterions are not present during polymerization to an extent detectable by ^1H NMR spectroscopy.

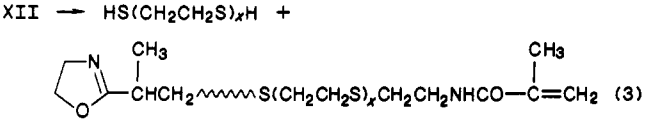
Polymerization Mechanism. Our results indicate the similarity of the $IPOH_2S$ and IPOEDT systems. Polymerization of the $IPOH_2S$ and IPOEDT adducts III and IV can be considered to proceed by the stepwise reaction of an AB type of bifunctional monomer (eq 2). The reaction involves nucleophilic ring-opening attack of sulfur to cleave the CH_2–O bond of the oxazoline ring. Growth proceeds to form different sized molecules of type XII, where x =



XII

0 and 1, respectively, for the $IPOH_2S$ and IPOEDT adducts. Zwitterions of types VII and XI and their counterparts derived from XII (formed by inter- or intramolecular proton transfer from SH to the nitrogen of the oxazoline ring) may be primarily responsible for the growth process. No evidence for the presence of zwitterions was found from ^1H NMR but that does not preclude their presence at low concentrations. Even low concentrations of such zwitterions would be important since RS^- and the protonated oxazoline ring are expected to be considerably more reactive as nucleophile and electrophile, respectively, compared to SH and the unprotonated oxazoline ring.

Elimination at the thiol end group of the growing polymer results in the formation of olefinic end groups (eq 3), where ~~~ represents the repeat unit of structure XII. The basicity of the oxazoline nitrogen (in the adduct and growing polymer) may be involved in promoting the elimination reaction.



(3)

The polymerization process is complicated by the decomposition of the $IPOH_2S$ and IPOEDT adducts as observed by the NMR detection of free IPO in the reaction products from bulk polymerization. It is assumed that adduct decomposition also occurs in solution polymerization although our workup procedure for isolation of the polymer precluded its detection. Free IPO and H_2S or EDT (the latter from both adduct decomposition and elimination reaction—eq 3) can add to the various polymer end groups—H_2S and EDT to oxazoline and olefinic end groups and IPO to thiol end groups. The relative extents of these and other reactions are different in the IPOEDT and $IPOH_2S$ systems.

Consider the IPOEDT system. The polymerization proceeds by the stepwise mechanism as evidenced by the increase in molecular weight with increasing reaction time and the $\bar{M}_w/\bar{M}_n$ values close to 2 (Table I). The molecular weight increases with increasing adduct concentration for solution polymerization. The molecular weight in bulk polymerization is lower than that for solution polymerization at adduct concentrations of 50% (w/w) and higher. This effect is attributed to a lowered molecular mobility in bulk polymerization which counteracts the higher adduct concentration. The extent of elimination increases with increasing reaction temperature with olefinic end groups predominating over thiol end groups at 160–170 °C. Further, the extent of elimination is greater for bulk polymerization than solution polymerization—apparently because the evolved 1,2-ethanedithiol can more easily escape from the reaction system.

Decomposition of IPOEDT adduct to IPO and EDT occurs to varying degrees depending on temperature. No free IPO was found below 140 °C or above 170 °C. IPOEDT decomposition is probably negligible below 140 °C. IPO and EDT may be involved in adding to thiol and oxazoline (and/or olefinic) end groups, respectively. Additional reaction possibilities for IPO include homopolymerization and/or copolymerization with olefinic end groups. The absence of free IPO in the reaction system above 170 °C probably does not indicate the absence of decomposition of IPOEDT adduct but the rapid con-

sumption of IPO by the various side reactions.

Bulk polymerization of IPOEDT adduct in the absence of the radical inhibitor BHA leads to cross-linking as detected by the formation of insoluble polymer. The obvious route to cross-linking is the polymerization of olefinic end groups and/or their copolymerization with IPO. The presence of BHA prevented cross-linking at all temperatures except 200 °C. Cross-linking did not occur in solution polymerization even in the absence of BHA.

The $IPOH_2S$ system differs from the IPOEDT system in some quantitative aspects. Decomposition of the adduct is more extensive for $IPOH_2S$, occurring at all reaction temperatures. The elimination reaction is also more extensive for the $IPOH_2S$ system. The greater volatility of H_2S relative to EDT is probably responsible for the greater extent of elimination and adduct decomposition. Liberated H_2S adds to oxazoline end grups to yield more thiol end groups than oxazoline end groups for solution polymerization at 160 °C. The thiol end groups are not detected due to their facile elimination to olefinic end groups. One observes the ratio of olefinic to oxazoline end groups to be greater than one. The outcome is somewhat different for bulk polymerizations. H_2S escapes the reaction system while the less volatile IPO remains and adds to thiol end groups. Oxazoline end groups constitute the major end groups at 100–120 °C. At higher reaction temperatures (140–160 °C), elimination of thiol end groups is favored over their reaction with IPO and the result is comparable amounts of oxazoline and olefinic end groups.

Small amounts of CH_2OH groups, identified in both the IPOEDT and $IPOH_2S$ polymers, are most likely formed by the reaction of oxazoline end groups with trace amounts of water present in the reaction mixture. The mechanism for forming CSSH groups, found in minor amounts in the $IPOH_2S$ polymer, is unclear.

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Registry No. IIIa, 32154-11-3; IIIa (homopolymer), 32070-33-0; IVa, 29920-38-5; IVa (homopolymer), 32070-18-1; Va, 28212-99-9; VIa, 110143-72-1; BHA, 489-01-0.

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Homogeneous Selective Catalytic Hydrogenation of C=C in Acrylonitrile–Butadiene Copolymer

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ABSTRACT: The chemical modification of unsaturated polymers via catalytic hydrogenation offers a potentially useful method for altering and optimizing the physical and mechanical properties of macromolecules. A study involving the hydrogenation of an acrylonitrile–butadiene copolymer has been carried out in the presence of $RhCl(P(C_6H_5)_3)_3$ which under mild reaction conditions provides quantitative hydrogenation of carbon–carbon unsaturation without any hydrogenation of the nitrile functionality. The selectivity of the catalyst for terminal versus internal double bonds present in the polymer is markedly influenced by the nature of the solvent media. In order to appreciate the important factors which influence the nature and extent of this reaction, a detailed kinetic study has been carried out under experimental conditions where the reaction is chemically controlled. The reaction kinetics exhibit unusual effects on substrate dependence and hydrogen dependence as well as solvent media. The kinetic results and spectral observations are consistent with a mechanism in which the active catalyst $RhClH_2(P(C_6H_5)_3)_2$ interacts with the carbon–carbon unsaturation within the copolymer in a rate-determining step. The nitrile functionality present in the copolymer also interacts with the active catalyst and inhibits the rate of hydrogenation.

Introduction

The development of new specialty polymers, from diene-based elastomers, with improved performance characteristics is of great importance in a number of product applications. This is primarily a result of the fact that the conditions to which well-established synthetic elastomers are currently being subjected to in the oil, nuclear power, and automotive industries have become much more severe in recent years.[1,2]

The chemical modification of unsaturated polymers via catalytic hydrogenation offers a potentially useful method for altering and optimizing the physical and mechanical properties of macromolecules. One of the major problems encountered, however, in such hydrogenation processes

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